

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 842 786 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

20.05.1998 Bulletin 1998/21

(51) Int. Cl.<sup>6</sup>: **B41M 5/00**

(21) Application number: **97119914.6**

(22) Date of filing: **13.11.1997**

(84) Designated Contracting States:

**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE**

Designated Extension States:

**AL LT LV MK RO SI**

(30) Priority: **15.11.1996 US 30997 P**

(71) Applicant:

**KIMBERLY-CLARK WORLDWIDE, INC.  
Neenah, Wisconsin 54956 (US)**

(72) Inventors:

- **Stokes, Bruce George  
Woodstock, GA 30188 (US)**
- **Zelazoski, Leonard Eugene  
Kennesaw, GA 30144 (US)**
- **Kronzer, Francis Joseph  
Woodstock, GA 30188 (US)**

(74) Representative:

**DIEHL GLAESER HILT & PARTNER  
Flügggenstrasse 13  
80639 München (DE)**

**(54) Print enhancement coating**

(57) A print enhancement coating which includes from 0 to 100 percent by weight of a polyvalent metal ion salt, from 0 to 100 percent by weight of a cationic polymer, and from 0 to 100 percent by weight of a viscosity modifier, all based on the total dry weight of the coating. The coating also may include a nonionic or cationic surfactant. When present, the ink viscosity modifier may be a poly(ethylene oxide) having a weight-average molecular weight of from about 10,000 to about 200,000 or a low to medium viscosity poly(vinyl alcohol) having a degree of hydrolysis of less than about 90 percent. In certain embodiments, the print enhancement coating may include from about 4 to about 90 percent by weight of a polyvalent metal ion salt and from about 96 to about 10 percent by weight of a cationic polymer. The present invention also provides a printable material which includes a first layer having a first side and a second side, a second layer overlaying the first surface of the first layer; and a third layer overlaying the second layer. The second layer includes particles of a thermoplastic polymer having largest dimensions of less than about 50  $\mu\text{m}$  and from about 10 to about 50 weight percent of a film-forming binder, based on the weight of the thermoplastic polymer. The third layer is the print enhancement coating described above.

**EP 0 842 786 A1**

## Description

The present invention relates to an ink jet printable material.

The popularity in recent years of personal computers in homes and businesses has stimulated the development of several types of printers. The earlier, relatively low cost printers were impact or dot-matrix printers which utilized a ribbon and a plurality of pins to place a desired image on a substrate which typically was paper. While the better dot-matrix printers are capable of near letter-quality printing, they typically are both slow and noisy. Laser printers are quiet, produce high-quality images, and can print an excess of four pages per minute. Such printers, however, tend to be too expensive for common use in homes and even in some smaller businesses; this is especially true for color laser printers. Ink jet printers fill the gap between dot-matrix printers and laser printers, both with respect to cost and image quality.

The advent of improved, relatively low cost color printers has aided the development of a significant industry which involves the application of customer-selected designs, messages, illustrations, and the like (referred to collectively hereinafter as "customer-selected graphics") on articles of clothing, such as T-shirts, sweat shirts, and the like. These customer-selected graphics typically are commercially available products tailored for that specific end-use and are printed on a release or transfer paper. They are applied to the article of clothing by means of heat and pressure, after which the release or transfer paper is removed.

Some effort has been directed to allowing customers the opportunity to prepare their own graphics for application to an article of clothing. The preparation of such graphics may involve the use of colored crayons made from a heat-transferable material. Such crayons have been made available in kit form, which also includes an unspecified heat transfer sheet having an outlined pattern thereon. In a variation of the kit, the transferable pattern is created from a manifold of a heat transfer sheet and a reverse or lift-type copy sheet having a pressure transferable coating of heat transferable material thereon. By generating the pattern or artwork on the obverse face of the transfer sheet with the pressure of a drafting instrument, a heat transferable mirror image pattern is created on the rear surface of the transfer sheet by pressure transfer from the copy sheet. The heat transferable mirror image then can be applied to a T-shirt or other article by heat transfer.

The creation of personalized, creative designs or images on a fabric such as a T-shirt or the like through the use of a personal computer system has been described. The method involves electronically generating an image, electronically transferring the image to a printer, printing the image with the aid of the printer on an obverse surface of a transfer sheet which has a final or top coating consisting essentially of Singapore Dammar Resin, positioning the obverse face of the transfer sheet against the fabric, and applying energy to the rear of the transfer sheet to transfer the image to the fabric. The transfer sheet can be any commercially available transfer sheet, the heat-transferable coating of which has been coated with an overcoating of Singapore Dammar Resin. The use of abrasive particles in the Singapore Dammar Resin coating also has been described. The abrasive particles serve to enhance the receptivity of the transfer sheet to various inks and wax-based crayons.

Additionally, improved heat transfer papers having an enhanced receptivity for images made by wax-based crayons, thermal printer ribbons, and impact ribbon or dot-matrix printers have been disclosed. For example, a cellulosic base sheet has an image-receptive coating containing from about 15 to about 80 percent of a film-forming binder and from about 85 to about 20 percent by weight of a powdered polymer consisting of particles having diameters from about 2 to about 50  $\mu\text{m}$ . The binder typically is a latex. Alternatively, a cellulosic base sheet has an image-receptive coating which typically is formed by melt extrusion or by laminating a film to the base sheet. The surface of the coating or film then is roughened by, for example, passing the coated base sheet through an embossing roll.

Some effort also has been directed at generally improving the transfer of an image-bearing laminate to a substrate. For example, an improved release has been described, in which upon transfer the release splits from a carrier and forms a protective coating over the transferred image. The release is applied as a solution and contains a montan wax, a rosin ester or hydrocarbon resin, a solvent, and an ethylene-vinyl acetate copolymer having a low vinyl acetate content.

Additional effort has been directed to improving the adhesion of the transferred laminate to porous, semi-porous, or non-porous materials, and the development of a conformable transfer layer which enables the melt transfer web to be used to transfer images to uneven surfaces.

It is well known by those having ordinary skill in the art that current ink jet inks are aqueous-based systems. That is, the dyes employed in such inks are soluble in water. Thus, substrates printed with ink jet inks have a pronounced proclivity to run or even lose an image in the presence of moisture or water. In addition, ink jet inks often have a tendency to spread after being placed on a substrate, a phenomenon referred to in the art as "bleeding," thereby adversely affecting the sharpness or resolution of the image. Moreover, customer-selected graphics produced by desk-top publishing software and printed by ink jet printers result in graphics which in general are not transferred satisfactorily by known heat transfer papers. This is particularly true when transfer is attempted with a hand-held iron.

It is therefore an object of the present invention to overcome the drawbacks and disadvantages of the prior art. Con-

sequently, there is an opportunity for an improved heat transfer paper which has been developed specifically for graphics printed with an ink jet printer, i.e., an ink-jet printable heat transfer paper. There also is an opportunity for an improved heat transfer paper which has improved durability, especially in the presence of water, and which results in a softer, more pliable transferred image. Finally, there is an opportunity for a material which, when printed on by an ink jet printer, has a reduced tendency to bleed.

The printable material according to independent claim 9 and the print enhancement coating according to independent claim 1 solve this object of the present invention.

Further advantageous features, aspects and details of the invention are evident from the dependent claims, description and examples. The claims are to be understood as a first, non-limiting approach to defining the invention in general terms.

The present invention addresses some of the difficulties and problems discussed above by providing a print enhancement coating which includes from 0 to 100 percent by weight of a polyvalent metal ion salt, from 0 to 100 percent by weight of a cationic polymer, and from 0 to 100 percent by weight of a viscosity modifier, all based on the total dry weight of the coating. The coating also may include a nonionic or cationic surfactant. For example, the surfactant may be a nonionic surfactant.

When present, the ink viscosity modifier may be a poly(ethylene oxide) having a weight-average molecular weight of from about 10,000 to about 200,000. As another example, the poly(ethylene oxide) may have a weight-average molecular weight of from about 20,000 to about 100,000. As further example, the ink viscosity modifier may be a low to medium viscosity poly(vinyl alcohol) having a degree of hydrolysis of less than about 90 percent.

In certain embodiments, the print enhancement coating may include from about 4 to about 90 percent by weight of a polyvalent metal ion salt and from about 96 to about 10 percent by weight of a cationic polymer. The coating also may include a nonionic or cationic surfactant. For example, the surfactant may be a nonionic surfactant. The coating also may include an ink viscosity modifier. For example, the ink viscosity modifier may be a poly(ethylene oxide) having a weight-average molecular weight of from about 10,000 to about 200,000. As another example, the poly(ethylene oxide) may have a weight-average molecular weight of from about 20,000 to about 100,000. As a further example, the ink viscosity modifier may be a low to medium viscosity poly(vinyl alcohol) having a degree of hydrolysis of less than about 90 percent.

The present invention also provides a printable material which includes a first layer having a first side and a second side, a second layer overlaying the first surface of the first layer; and a third layer overlaying the second layer. The second layer includes particles of a thermoplastic polymer having largest dimensions of less than about 50  $\mu\text{m}$  and from about 10 to about 50 weight percent of a film-forming binder, based on the weight of the thermoplastic polymer. The third layer includes from 0 to 100 percent by weight of a polyvalent metal ion salt, from 0 to 100 percent by weight of a cationic polymer, and from 0 to 100 percent by weight of a viscosity modifier, all based on the total weight of the third layer.

As used herein, the term "print enhancement" refers to the prevention or reduction of bleeding in images printed by an ink jet printer.

The term "polyvalent metal ion salt" means an organic or inorganic salt of a polyvalent metal ion. The term "polyvalent metal" includes metals in Groups 2-13 of the Periodic Table of the Elements (new notation). For example, the polyvalent metal may be a metal of Groups 2, 12, and 13. As another example, the metal may be magnesium, calcium, zinc, or aluminum. Desirably, the polyvalent metal ion salt will be an inorganic salt.

As used herein, the term "cationic polymer" means a polymer containing a plurality of cationic groups. By way of example, the cationic polymer may be an amide-epichlorohydrin polymer, polyacrylamides with cationic functional groups, polyethyleneimines, polydiallylamines, polyacrylates and polymethacrylates in which the ester portions contain quaternary ammonium groups, and the like. Desirably, the cationic polymer will be a polyacrylate or a polymethacrylate in which the ester portion is a tetraalkylammonium group.

The print enhancement coating provided by the present invention includes from 0 to 100 percent by weight of a polyvalent metal ion salt, from 0 to 100 percent by weight of a cationic polymer, and from 0 to 100 percent by weight of a viscosity modifier, all based on the total dry weight of the coating. For example, the print enhancement coating may include from about 4 to about 90 percent by weight of a polyvalent metal ion salt and from about 96 to about 10 percent by weight of a cationic polymer, all based on the total dry weight of the coating.

The print enhancement coating may include a nonionic or cationic surfactant. Examples of nonionic surfactants, include, by way of illustration only, alkyl poly-ethoxylates, polyethoxylated alkylphenols, fatty acid ethanol amides, complex polymers of ethylene oxide, propylene oxide, and alcohols, and polysiloxane polyethers. Cationic surfactants include, again by way of illustration, tallow trimethylammonium chloride. Desirably, the surfactant will be a nonionic surfactant.

When present in the print enhancement coating, the ink viscosity modifier may be a poly(ethylene oxide) having a weight-average molecular weight of from about 10,000 to about 200,000. As another example, the poly(ethylene oxide) may have a weight-average molecular weight of from about 20,000 to about 100,000. As still another example, the ink

viscosity modifier may be a low to medium viscosity poly(vinyl alcohol) having a degree of hydrolysis of less than about 90 percent.

The present invention also provides a printable material which includes a first layer having a first side and a second side, a second layer overlaying the first surface of the first layer; and a third layer overlaying the second layer. The second layer includes particles of a thermoplastic polymer having largest dimensions of less than about 50  $\mu\text{m}$  and from about 10 to about 50 weight percent of a film-forming binder, based on the weight of the thermoplastic polymer.

In general, the first layer can be any material adapted for the end-use desired. The first layer typically will be a sheet material, more typically a flexible sheet material. Examples of flexible sheet materials include films, papers, nonwoven and woven webs, foils, and the like.

When the printable material is intended for use as a heat-transfer material, the first layer often will be a film or a paper. An example of a suitable film is a biaxially oriented film having a typical thickness of about 76  $\mu\text{m}$  (3 mils). This type of film typically is used to make transparencies for overhead projectors. When a paper is employed as the first layer, the thickness of the paper desirably will be from about 76 to about 152  $\mu\text{m}$  (from about 3 to about 6 mils). An especially useful paper is a label paper having what is referred to in the art as a print coating on one side. The print coating typically is a latex binder containing clay and starch, as is also well known in the art. The second layer usually is applied to the side of the paper not having the print coating, although the paper may have a print coating on both sides. While thinner or thicker papers may be used, the paper should have sufficient strength for handling, coating, sheeting, and other operations associated with its manufacture, and for removal after transferring an image. Other papers which may be used are latex-saturated papers.

As already noted, the second layer includes particles of a thermoplastic polymer having largest dimensions of less than about 50  $\mu\text{m}$ . Desirably, the particles will have largest dimensions of less than about 20  $\mu\text{m}$ . In general, the thermoplastic polymer can be any thermoplastic polymer which meets the criteria set forth herein. For example, the powdered thermoplastic polymer may be a polyolefin, polyester, polyamide, copolyamide, or ethylene-vinyl acetate copolymer.

The second layer also includes from about 10 to about 50 weight-percent of a film-forming binder, based on the weight of the thermoplastic polymer. Desirably, the amount of binder will be from about 10 to about 30 weight percent. In general, any film-forming binder may be employed which meets the criteria set forth herein. Suitable binders include polyacrylates, polyethylenes, and ethylene-vinyl acetate copolymers. The binder desirably will be heat softenable at temperatures of about 120° Celsius or lower.

The basis weight of the second layer may vary from about 5 to about 30 grams per square meter ( $\text{g}/\text{m}^2$ ). Desirably, the basis weight will be from about 10 to about 20  $\text{g}/\text{m}^2$ . The second layer can be applied to the first layer, either directly or over a third or other layer, by means well known to those having ordinary skill in the art. For example, the layer may be applied by Meyer rod, air knife, and gravure coating, by way of illustration only.

When the printable material is intended to be used as a heat-transfer material, the second layer will have a melting point of from about 65 to about 180° Celsius. The term "melts" and variations thereof are used herein only in a qualitative sense and are not meant to refer to any particular test procedure. Reference herein to a melting temperature or range is meant only to indicate an approximate temperature or range at which a polymer or binder melts and flows under the conditions of a melt-transfer process to result in a substantially smooth film.

Manufacturers' published data regarding the melt behavior of polymers or binders correlate with the melting requirements described herein. It should be noted, however, that either a true melting point or a softening point may be given, depending on the nature of the material. For example, materials such as polyolefins and waxes, being composed mainly of linear polymeric molecules, generally melt over a relatively narrow temperature range since they are somewhat crystalline below the melting point.

Melting points, if not provided by the manufacturer, are readily determined by known methods such as differential scanning calorimetry. Many polymers, and especially copolymers, are amorphous because of branching in the polymer chains or the side-chain constituents. These materials begin to soften and flow more gradually as the temperature is increased. It is believed that the ring and ball softening point of such materials, as determined by ASTM E-28, is useful in predicting their behavior in the present invention. Moreover, the melting points or softening points described are better indicators of performance in this invention than the chemical nature of the polymer or binder.

Finally, the third layer is the print enhancement coating described hereinbefore. In general, the print enhancement coating or the third layer will have a basis weight of from about 0.1 to about 5  $\text{g}/\text{m}^2$ .

For heat transfer applications, the printable material desirably will have an additional layer which may be, for example, a release layer or a melt-transfer film layer. Additional layers may be included, if desired. Such additional layer or layers, if used, typically will be located between the first layer and the second layer.

A melt-transfer film layer typically comprises a film-forming binder, as already described, or other polymer. The layer desirably is applied by extrusion coating, but other methods also may be used. The melt-transfer film layer desirably is formed from a polyethylene or a copolymer of ethylene with acrylic acid, methacrylic acid, vinyl acetate, or acrylic acid esters such as ethyl acrylate. The polymer desirably will have a melt flow rate of at least about 30 grams per 10

minutes (g/10 minutes), as determined in accordance with ASTM Method D-1238), although the melt flow rate may be as high as about 4,000 g/10 minutes. More desirably, the melt flow rate of the polymer will be from about 300 to about 700 g/10 minutes. The basis weight of the melt-transfer film layer desirably will be from about 10 to about 50 grams per square meter (g/m<sup>2</sup>), with a basis weight of from about 30 to about 50 being more desired.

A release layer may be included, either in place of or in addition to the melt-transfer film layer. In the former instance, the release layer will be placed between the first layer and the second layer. In the latter instance, the release layer will be placed between the first layer and the melt-transfer film layer. The latter is particularly desired when heat transfer will be accomplished by means of a hand-held iron. The release layer desirably will be a low molecular weight ethylene-acrylic acid copolymer applied from an aqueous dispersion. The melt flow rate of the ethylene-acrylic acid copolymer desirably will be at least about 200 g/10 minutes, more desirably from about 800 to about 1,200 g/10 minutes. Such dispersion also may contain a paraffin wax, which is mixed as an emulsion with the ethylene-acrylic acid copolymer dispersion. The paraffin wax emulsion can be any of those which are commercially available, such as Chemawax<sup>®</sup> 40 (Chematron, Inc., Charlotte, North Carolina). The ratio of paraffin wax to the copolymer may vary from 0 to about 4, with a ratio of about 1 being more desirable. The basis weight of the release layer desirably will be from about 2 to about 20 g/m<sup>2</sup>, more desirably from about 6 to about 10 g/m<sup>2</sup>. The release coating as described melts easily and provides easy release from the first layer for hand ironing of images onto a fabric; such characteristic is especially useful if heating of the image is irregular, which is not atypical of hand-ironing techniques.

The second and any additional desired layers are formed by known coating techniques, such as by roll, blade, and air-knife coating procedures. The resulting material then is dried by means of, for example, steam-heated drums, air impingement, radiant heating, or some combination thereof. Some care must be exercised, however, to assure that drying temperatures are sufficiently low so that the particles of thermoplastic polymer present in the second layer do not melt during the drying process. Air impingement for 5 minutes or more at 80° Celsius was used successfully.

Heat transfer of an image printed on the printable material of the present invention may be by any known means, such as by a hand-held iron or a heat transfer press. The latter is desired, however. The transfer temperature typically will be from about 120° to about 205° Celsius, for from about 5 seconds to about 2 minutes. A temperature of about 160° Celsius for about 15 seconds generally works well.

The present invention is further described by the examples which follow. Such examples, however, are not to be construed as limiting in any way either the spirit or the scope of the present invention.

#### Examples I-XXIII and Comparative Examples I and II

The first layer in the examples, unless otherwise stated, was a commercially available print-coated heat transfer paper. The base paper was coated first by melt extrusion with an about 46- $\mu$ m (1.8-mil) layer of a 500 melt index ethylene-methacrylic acid copolymer (Nucrel<sup>®</sup> 599). This melt-extruded layer then was coated with a layer composed of about 75 weight-percent of polyamide particles (Orgasol<sup>®</sup> 3501 EXD NAT1, a 10- $\mu$ m average particle size copolymer of  $\epsilon$ -caprolactam and laurilactam, having a melting point of 160°C and available from Elf Atochem, France), about 19 weight-percent of an ethylene-acrylic acid copolymer (Miche<sup>®</sup> Prime 4983), and about 4 weight-percent of a polyethoxylated octylphenol nonionic surfactant (Triton<sup>®</sup> X-100, Rohm & Haas Co., St. Louis, Missouri). Miche<sup>®</sup> Prime 4983 was a 25 percent solids dispersion of Primacor<sup>®</sup> 5983 made by Dow Chemical Company. The polymer contained 20 percent acrylic acid and 80 percent ethylene. The copolymer had a Vicat softening point of 43°C and a ring and ball softening point of 100°C. The melt flow rate of the copolymer was 500 g/10 minutes. The basis weight of the coating was about 14 g/m<sup>2</sup>.

Print testing was carried out with a Canon BJ 4200 printer with the BC 22 photo ink cartridge. The cartridge enables the user to select color photo graphics. The test print employed in the examples was an image having a woman's face as well as colored squares of cyan, yellow, magenta, red, blue, green, and black. Heat transfers, when done, were to a 100 percent cotton T-shirt material. Wash tests, when done, were in a home laundry using commercial detergent on the warm/warm cycle. The heat transfer press conditions were 177° C for 20 seconds.

A variety of print-enhancement coatings were studied. They are summarized in Table I. The print, transfer, and wash test results are summarized in Table 2. In Table 2, the control was a sheet of the print-coated heat transfer paper which had not been coated with a print enhancement layer.

Table I

Descriptions of Examples	
Example	Description
EI	0.15 gsm (g/m <sup>2</sup> ) of Airvol <sup>®</sup> 523, a partially hydrolyzed poly(vinyl alcohol) (from 5% solution).

Table I (continued)

Descriptions of Examples	
Example	Description
EII	0.5 g/m <sup>2</sup> of Airvol <sup>®</sup> 523.
EIII	0.3 g/m <sup>2</sup> of 50/50 blend of Airvol <sup>®</sup> 523 and SMA 1440H (an ammonia neutralized styrene-maleic acid copolymer), from a 10 weight-percent solution.
EIV	0.9 g/m <sup>2</sup> of 50/50 Airvol <sup>®</sup> 523/SMA 1440H.
EV	0.25 g/m <sup>2</sup> of Polyox <sup>®</sup> N60K [poly(ethylene oxide)], from a 2.5 weight-percent solution.
EVI	0.5 g/m <sup>2</sup> of 50/50 Polyox <sup>®</sup> N60K/trisodium phosphate.
EVII	0.5 g/m <sup>2</sup> of 50/50 Polyox <sup>®</sup> N60K/ammonium benzoate.
EVIII	0.5 g/m <sup>2</sup> of 50/50 Polyox <sup>®</sup> N60K/aluminum sulfate hexadecahydrate.
EIX	0.1 g/m <sup>2</sup> of aluminum sulfate hexadecahydrate.
EX	0.7 g/m <sup>2</sup> of aluminum sulfate hexadecahydrate.
EXI	0.4 g/m <sup>2</sup> of Alcostat <sup>®</sup> 567 [poly(trimethylethylammonium methacrylate)], chloride salt, from Allied Colloids.
EXII	0.8 g/m <sup>2</sup> of Alcostat <sup>®</sup> 567.
EXIII	A 7.5 weight-percent total solids blend of Polyox <sup>®</sup> N60K, Alcostat <sup>®</sup> 567 and Triton <sup>®</sup> X-100 in a 0.8/1.0/0.8 weight ratio, 2.5 g/m <sup>2</sup> .
EXIV	A 10 weight-percent total solids blend of Airvol <sup>®</sup> 523, Alcostat <sup>®</sup> 567 and Triton <sup>®</sup> X-100 in a 1/1/0.2 weight ratio, 3 g/m <sup>2</sup> .
EXV	Calcium chloride tetrahydrate, 1.5 g/m <sup>2</sup> .
EXVI	Magnesium acetate hexahydrate and Triton <sup>®</sup> X-100, 1/0.2/ 1.5 g/m <sup>2</sup> .
EXVII	Zinc acetate dihydrate, 1.5 g/m <sup>2</sup> .
EXVIII	2.2 g/m <sup>2</sup> , 2/1/0.2 weight ratio of hydrated calcium chloride/Alcostat <sup>®</sup> 5667, Triton <sup>®</sup> X-100.
EXIX	3 g/m <sup>2</sup> , 1/1/0.1 weight ratio of hydrated calcium chloride/ Alcostat <sup>®</sup> 567, Triton <sup>®</sup> X-100.
EXX	2.2 g/m <sup>2</sup> , 1/1/0.1/0.02 weight ratio of Alcostat <sup>®</sup> 567, Airvol <sup>®</sup> 523, zinc acetate dihydrate, and Triton <sup>®</sup> X-100.
EXXI	3 g/m <sup>2</sup> , 1/1/0.3/0.15 weight ratio of Alcostat <sup>®</sup> 567, Airvol <sup>®</sup> 523, zinc acetate dihydrate and Triton <sup>®</sup> X-100.
EXXII	1.5 g/m <sup>2</sup> , 1/0.1 weight ratio of Alcostat <sup>®</sup> 567 and Triton <sup>®</sup> X-100.
EXXIII	1.5 g/m <sup>2</sup> , 1/0.6 weight ratio of aluminum sulfate hexadecahydrate and Alcostat <sup>®</sup> 567.
CEI	This is a comparative example without an overcoat. The paper was extrusion coated with about 18 $\mu$ m (0.7 mil) of Nucrel <sup>®</sup> 599. The print coat was a 100/10/10/5 blend of dispersed Orgasol <sup>®</sup> 3501 EXD NAT I, Airvol <sup>®</sup> 523, Alcostat 567 and Triton <sup>®</sup> X-100. This was applied at 25% total solids to give a coating weight of 14 g/m <sup>2</sup> . Note that the coating does not contain Michem <sup>®</sup> 4983 binder.
CEII	This comparative example was like CEI, except that the Nucrel <sup>®</sup> 599 film was about 38 $\mu$ m (1.5 mils) thick.

Table II

Print, Transfer, and Wash Test Results					
Example	Print Resolution <sup>a</sup>	Print Color	Color Shift <sup>b</sup>	Transfer	Wash Test
Control	Very poor	Greyish	Green	Good	----
EI	Poor	Greyish	Green	Good	Good
EII	Fair	Greyish	Green	Good	Good
EIII	Poor	Greyish	green	Good	Good
EIV	Fair	Greyish	Green	Good	Good
EV	Good	Good	Green	Good	Good
EVI	Good	Good	Green	Good	Good
EVII	Good	Reddish	Green	Good	Good
EVIII	Good	Good	Green	Good	Good
EIX	Fair	Greyish	Yellow	Good	Good <sup>c</sup>
EX	Excellent	Good	Yellow	Good	Good <sup>c</sup>
EXI	Fair	Good	Very slight yellow	Good	Good
EXII	Good	Good	Very slight yellow	Good	Good
EXIII	Very Good	Good	Very slight yellow	Good	Good
XIV	Very good	Good	Very slight yellow	Good	Very Good
EXV	<sup>d</sup>	Blue	None	Good	Poor <sup>d</sup>
EXVI	Poor <sup>e</sup>	Good	----	Very poor	----
EXVII	Note <sup>f</sup>	Good	Less yellow	Poor	Good
EXVIII	Good	Blue	Green	Good	Fair
EXIX	Excellent	Blue	Slight green	Good	Excellent
EXX	Good	Good	Good	Good	Fair
EXXI	Good	Good	Good	Good	Excellent
EXXII	Good	Good	Good	Good	Good
EXXIII	Excellent	Good	Yellow	Good	Excellent <sup>g</sup>
CEI	Good	Good	Slight yellow	Good	Very poor
CEII	Good	Good	Slight yellow	Good	Very poor

<sup>a</sup> Resolution as a function of color bleeding (the greater the bleeding, the lower the resolution).

<sup>b</sup> After transfer.

<sup>c</sup> The yellow color persisted after washing.

<sup>d</sup> Dye bleed was stopped for all but the cyan dye, which left a blue halo. Sample turned very blue after washing.

<sup>e</sup> yellow dye bleed stopped, but other colors bled.

<sup>f</sup> Black and yellow dye bleed stopped, but other colors bled.

<sup>g</sup> Yellowness disappeared after washing, giving excellent results.

#### Example XXIV

An about 178- $\mu$ m (7-mil) ink jet paper, extrusion coated with polyethylene on both sides, with a glossy front side and a matte back side, was used for this example. The paper was obtained from Jen Coat, Inc., Westfield, Massachusetts.

The paper was coated on the front side with a 100/25/5/5 parts by weight blend of Orgasol® 3501 EXD NAT 1, Michem® Prime 4983, Airvol® 523, and SMA 1440H (a styrene-maleic anhydride copolymer dispersant from Elf Atochem). The coating basis weight was about 16 g/m<sup>2</sup>. The coating total solids content was 27 weight-percent. A second coating was applied, utilizing a solution of a 100/100/5 parts by weight ratio of Alcostat® 567, Airvol® 523, and Tergitol® 15-S-9, a secondary alcohol polyethoxylate.

The resulting material was printed, then fused, using a 0.5 Mylar polyester film on the print side and a release paper on the backside, in a Hix heat transfer press at about 132°C for 30 seconds. The image was the same as the one used for Examples I-XXIII and Comparative Examples I and II. The image was glossy, water resistant, and looked much like a glossy photograph.

While the specification has been described in detail with respect to specific embodiments thereof, it will be appreciated by those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

## Claims

1. A print enhancement coating which comprises:

from 0 to 100 percent by weight of a polyvalent metal ion salt;

from 0 to 100 percent by weight of a cationic polymer; and

from 0 to 100 percent by weight of a viscosity modifier;

all based on the total dry weight of the coating.

2. The print enhancement coating of claim 1 which further comprises a nonionic or cationic surfactant.

3. The print enhancement coating of claim 1 or 2, in which the surfactant is a nonionic surfactant.

4. The print enhancement coating of any of the preceding claims which further comprises an ink viscosity modifier.

5. The print enhancement coating of claim 4, in which the ink viscosity modifier is a poly(ethylene oxide) having a weight-average molecular weight of from about 10,000 to about 200,000.

6. The print enhancement coating of claim 5, in which the poly(ethylene oxide) has a weight-average molecular weight of from about 20,000 to about 100,000.

7. The print enhancement coating of claim 4, in which the ink viscosity modifier is a low to medium viscosity poly(vinyl alcohol) having a degree of hydrolysis of less than about 90 percent.

8. The print enhancement coating of any of the preceding claims which comprises:

from about 4 to about 90 percent by weight of a polyvalent metal ion salt; and

from about 96 to about 10 percent by weight of a cationic polymer;

all based on the total dry weight of the coating.

9. A printable material comprising:

a first layer having a first side and a second side;

a second layer overlaying the first surface of the first layer; and

a third layer overlaying the second layer;  
wherein



the second layer comprises particles of a thermoplastic polymer having largest dimensions of less than about 50  $\mu\text{m}$  and from about 10 to about 50 weight percent of a film-forming binder, based on the weight of the thermoplastic polymer; and

the third layer comprises from 0 to 100 percent by weight of a polyvalent metal ion salt and from 100 to 0 percent by weight of a cationic polymer, all based on the total dry weight of the layer.

10. The printable material of claim 9 which further comprises a nonionic or cationic surfactant.

11. The printable material of claim 10, in which the surfactant is a nonionic surfactant.

12. The printable material of any of the preceding claims which further comprises an ink viscosity modifier.

13. The printable material of claim 12, in which the ink viscosity modifier is a poly(ethylene oxide) having a weight-average molecular weight of from about 10,000 to about 200,000.

14. The printable material of claim 13, in which the poly(ethylene oxide) has a weight-average molecular weight of from about 20,000 to about 100,000.

15. The printable material of claim 12, in which the ink viscosity modifier is a low to medium viscosity poly(vinyl alcohol) having a degree of hydrolysis of less than about 90 percent.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 97 11 9914

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	US 5 501 902 A (KRONZER FRANCIS J) * column 8, line 29 - line 50 * * claims * * the whole document *	9-14	B41M5/00
X	EP 0 199 874 A (MEAD CORP) * page 6, line 1 - page 9, line 18 * * examples 1,2 * * the whole document *	1,5,6,8	
Y	---	9-14	
X	EP 0 164 196 A (MEAD CORP) * claims 1-3,6,18,22 * * examples * * page 14, line 17 - line 22 * * the whole document *	1,2,4,8	
X	DATABASE WPI Week 9439 Derwent Publications Ltd., London, GB; AN 94313378 XP002056115 & JP 06 239 015 A (OJI PAPER CO) , 30 August 1994 * abstract *	1,5,6	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X	EP 0 184 797 A (POLAROID CORP) * claims; tables * * the whole document *	1	B41M
X	EP 0 704 316 A (EASTMAN KODAK CO) * claims 1,5,22 * * the whole document *	1	
X	GB 2 147 003 A (RICOH KK) * claims 1,3,5,10,11 * * the whole document *	1	
	--- -/--		
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		18 February 1998	Martins Lopes, L
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03 82 (P04C01)



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 97 11 9914

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X,P	WO 97 01447 A (KIMBERLY CLARK CO) * page 6, line 14 - line 29 * * example 1 * * claim 1 * * the whole document * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>18 February 1998</b>	Examiner <b>Martins Lopes, L</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  .....  &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/82 (P04C01)

THIS PAGE BLANK (USPTO)